



## Study of TATP: Method for determination of residual acids in TATP

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### ABSTRACT

Triacetone triperoxide (3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexoxonane, TATP) is nowadays one of the most commonly used improvised explosives. It is prepared by the action of hydrogen peroxide on acetone in an acidic environment. Easily available mineral acids – hydrochloric, sulfuric, nitric and perchloric – are the most often recommended on the extremist web pages dealing with improvised production of explosives. The various TATP producers' choice of acid mainly depends on the author's experiences and the local availability of the acid. A knowledge of the kind of acid used for TATP production can help in detecting the person who has made the TATP, or who has committed a criminal act using TATP. Therefore, a capillary isotachophoretic method was developed for determination of residual anions (originating from the acid used during TATP synthesis) in the resulting TATP crystals. This analytical method has proved to be reliable; the acid used for TATP synthesis was correctly identified in all samples analyzed.

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### 1. Introduction

Triacetone triperoxide (3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexoxonane, TATP) is currently one of the most synthesized and misused improvised explosives. One of the first published abuses of this compound was reported by Zitrin, Kraus and Glattstein in Israel [1]. These authors reported TATP as an unusual and rare explosive used for terrorist activity at that time. Unfortunately, some 30 years later, TATP has become one of the most common improvised explosives used by young chemists, criminals and terrorists throughout the world [2–4]. Probably the most well-known abusive use of TATP was by Richard Reid who used it as a primary explosive in his shoe bomb in the attempted bombing of a US airliner in December 2001 [4]. The reason why TATP is used so much is its simple synthesis procedure; knowledge of the synthesis is widespread and available via internet; ingredients for synthesis are easily available in the chemical trade networks or do-it-yourself markets without any restrictions on the sale of such substances [5].

In improvised conditions, TATP is always prepared by reaction of acetone with hydrogen peroxide in an acidic environment. The various acids published on web pages for preparing TATP as an improvised explosive depend on the particular author of the procedure and his experiences, and on local availability of the acid.

The acid used has not only an impact on product composition [6–8] but also on the properties of the TATP synthesized [9]. A small amount of the acid used as a catalyst during TATP preparation remains in the crude TATP even though thorough washing of the TATP crystals is carried out after preparation. As we reported in our previous studies, the residues of acid have a strong impact on TATP's properties (thermal stability [10]; transformation of TATP to 3,3,6,6-tetramethyl-1,2,4,5-tetraoxane (known under the acronym DADP) [11,12]; stability of TATP in solutions [13]). The residual acid can be quantified by titration. Unfortunately, the published analytical procedure can only determine the level of acidity ( $H^+$  ions) and not the specific anions [10].

The aim of this work was to utilize capillary isotachophoresis for determining the kind of residual anions in crude TATP, thereby determining the acid used in TATP preparation. This method can be utilized for forensic analysis of TATP, because TATP is usually not purified by re-crystallization in improvised conditions and the acid remains in the crude TATP. A knowledge of the acid used for TATP production can contribute to discovery of who has produced the explosive or who has used it for criminal purposes.

### 2. Materials and methods

*Caution: TATP is a primary explosive sensitive to impact, friction, electric discharge and flame even when wet. The synthesis and handling of TATP are dangerous operations that require standard safety precautions for handling primary explosives!!!*

#### 2.1. TATP synthesis

Triacetone triperoxide was synthesized by procedures that are published in various modifications on web pages dealing with improvised explosives. It was

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prepared by the standard route from acetone and hydrogen peroxide catalyzed using four different acids – 37% hydrochloric acid; 31% sulfuric acid; 65% nitric acid; and 70% perchloric acid. Altogether six batches of TATP were prepared using each acid mentioned (giving in total 24 batches). The molar ratio of acid to acetone was always 0.25. The synthesis details have already been published in our previous work (weights were one-tenth of original procedure) [14]. None of the TATP samples was purified by re-crystallization.

## 2.2. Preparation of solutions for analysis

For preparing the aqueous solutions containing residual acidity, extraction of highly concentrated toluene solutions of TATP with water was used. Desiccation of toluene solutions leads to formation of a crystalline crust of TATP, which therefore represents a certain risk when handling toluene TATP solutions. The crust is highly sensitive to various external mechanical impulses, and thus it is essential to prevent desiccation of such solutions. Laboratory glass equipment which has been in contact with TATP solutions must be thoroughly washed with ethanol or acetone immediately after use. The washings, together with any toluene TATP-containing residues from the extraction analysis, should be collected in a special container. However, should desiccation occur and the solid TATP crust be formed, it should be washed away immediately. Collected TATP-containing residues can be safely disposed of by incineration in an open container at a suitable place where people and the neighborhood are not exposed to any explosion or fire risk. This procedure has been examined and published by Bellamy [15]. Only people experienced in working with TATP or explosives in general should be allowed to handle TATP (such as weighing, extraction, laboratory equipment washing, incineration of residues, etc.). Undesirable explosion risk is minimized as long as all safety precautions are respected. We have successfully prepared and analyzed more than a 100 TATP samples.

About 1–1.5 g of TATP (precisely weighed) was dissolved in 10 ml toluene and then extracted with 10 ml distilled water (precisely measured using a pipette). Extraction time is about 15 min. Then the mixture was poured into a separating funnel with a well greased stopcock. Good lubrication is very important for elimination of any TATP ignition risk from excessive friction inside the stopcock during turning. The aqueous extract was then separated and analyzed by isotachopheresis.

## 2.3. Isotachopheresis

**Chemicals:** All chemicals used for isotachopheresis analysis were of analytical reagent grade. Hydrochloric acid, acetic acid, citric acid, sodium perchlorate, sodium sulfate, sodium nitrate, sodium chloride and cadmium nitrate were from Lachema (Brno, Czech Republic). D,L Histidine and 1,3-bis[tris-(hydroxymethyl)-methylamino]propane were obtained from Sigma (St. Louis, USA), hydroxyethyl cellulose 4000 (HEC) from Serva (Heidelberg, Germany). Standard solutions were prepared from de-ionized and redistilled water.

**Instruments and parameters for isotachopheretic analysis:** Capillary isotachopheresis experiments were performed in an Isotachopheretic Analyser (Villa Labeco, Spišská Nová Ves, Slovakia) equipped with a column coupling system consisting of two polytetrafluorethylene capillaries. The first, pre-separation, capillary (130 mm × 0.8 mm I.D.) was connected to the analytical capillary (180 mm × 0.3 mm I.D.) via the bifurcation block which enables determining the macro-components and micro-components of the samples. Both columns contained a conductivity detector. Sample volume was 35 µl. The driving current for the pre-separation capillary was 250 µA. For determining the  $\text{SO}_4^{2-}$ ,  $\text{ClO}_4^-$  and  $\text{NO}_3^-$  anions the electrolyte systems consisted of a leading electrolyte (LE) – 10 mM  $\text{Cl}^-$ , 20 mM  $\text{His}^+$ , 5 mM 1,3-bis[tris(hydroxymethyl)methylamino]propane, 1% hydroxyethyl cellulose (HEC), pH 5.8 and a terminating electrolyte (TE) – 10 mM acetic acid. Determining chloride anions was carried out using 5 mM  $\text{Cd}(\text{NO}_3)_2$  and 1% HEC – LE, and 10 mM citric acid – TE.

## 2.4. Experimental approach, verification of results

Experiments were performed using blind scenarios. All samples of TATP were prepared, and the subsequent water extraction carried out, by the synthesist. The water solutions of anions were then passed to the analyst without revealing any information about the synthesis method. In this way the analyst was always ignorant of any expected results. This was the approach used in order to verify the reliability of the method for determining the type of acid.

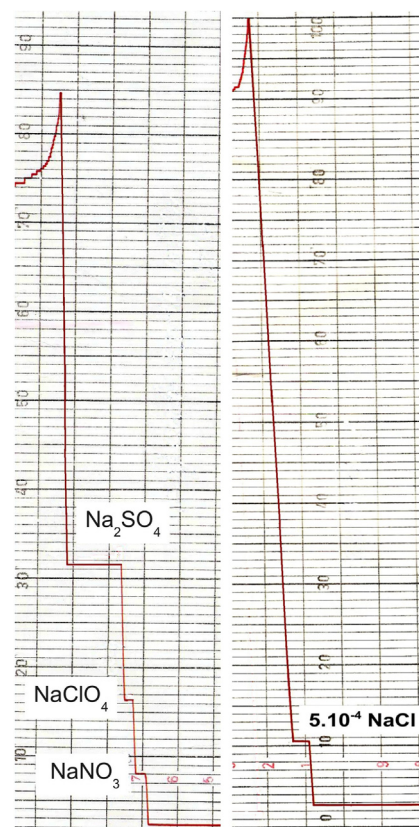
## 3. Results and discussion

Capillary isotachopheresis is a separation method very suitable for determining the presence of ionic substances. Identification of ionic species is based on the position of zones. The positions of the unknown zones are compared with the positions of zones occupied

by standards. It is a reliable and selective method for analyzing mixtures. Isotachopheretic analysis also allows quantification of ionic substances present, using the length of the zones.

For determining the following anions –  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{ClO}_4^-$  – it is necessary to choose a suitable electrolytic system consisting of a leading electrolyte, the anions of which must have a mobility that is higher than that of any of the sample anionic species, and a terminating electrolyte, the anions of which must have a mobility that is lower than all sample anions. The cations of the leading electrolyte should also have a buffering capacity at the pH at which the analyses will be performed. For this project, two electrolytic systems were used. The one for determining nitrates, sulfates and perchlorates consisted of 10 mM hydrochloric acid and 1,3-bis[tris(hydroxymethyl)methylamino]propane and histidine as the counter ions with pH 5.8. The terminating ions were acetates. The other operational system, for determining chlorides, consisted of 10 mM nitrates and  $\text{Cd}^{2+}$  ions as the counter ions. The terminating ions were citrates.

Isotachopherograms of the test mixtures of the anions studied are given in Fig. 1. From these figures it can be seen that the zones are well separated and identification of anions is assured. The dependences of zone lengths of a particular anion on its concentration are linear and were statistically evaluated by linear regression using the program ADSTAT (Trilobite s.r.o., Pardubice 1995). The statistical results found (limit of quantification and limit of detection) are summarized in Table 1.



**Fig. 1.** Isotachopherogram of the separation of model mixture of nitrates, perchlorates, sulfates and chlorides. Nitrates, perchlorates and sulfates were analyzed in the operational system at pH 5.8, with 10 mM HCl and 1,3-bis[tris(hydroxymethyl)methylamino]propane and histidine as the counter ions (left isotachopherogram). The terminating ions were acetates. Chlorides were analyzed in the operational system with 10 mM nitrates and cadmium as the counter ions (right isotachopherogram). The terminating ions were citrates.

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